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METHOD FOR MANUFACTURING ALUMINUM VAPOR-DEPOSITED MATERIALS

Masatoshi Iwai, et al.

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METHOD FOR MANUFACTURING ALUMINUM VAPOR-DEPOSITED MATERIALS

[Aruminyumukei jyouchaku mekkizai no seizouhoho]

Inventors:	Masatoshi Iwai Junji Kawafuku Koji Irie Tota Ayabe Shoji Miyake
Applicant:	000001199 Kobe Steel Ltd.

Claims

1. In vacuum vapor deposition method in which Al vapor deposition is continuously carried out at least on one side of a pretreated substrate, the method for manufacturing Al vapor-deposited materials is characterized by satisfying the following three conditions simultaneously,

(1) the residual hydrogen gas content in the vapor deposition chamber is 90 vol% or greater based on the total residual gas in the vapor deposition chamber,

(2) among the residual gas in the vapor deposition chamber, the sum of the partial pressure of moisture, oxygen, carbon monoxide, and carbon dioxide gas is 1×10^{-3} Pa or less,

(3) the temperature T ($^{\circ}\text{C}$) of the substrate at the beginning of the vapor deposition satisfies the following condition

$$150^{\circ}\text{C} \leq T \leq 400^{\circ}\text{C}.$$

2. Method for manufacturing Al vapor-deposited materials described in Claim 1, characterized in that as a pretreatment of the substrate, the substrate is heated in a reducing gas atmosphere to carry out reduction and activation of the substrate surface, followed by cooling to the specified temperature in a nonoxidizing atmosphere, then the substrate is introduced into a vapor deposition chamber to continuously carry out Al vapor deposition on at least one side of the substrate.

Detailed explanation of the invention

[0001]

Industrial application field

The present invention pertains to an Al vacuum vapor deposition method using electron-beam heating. More precisely, it pertains to a manufacturing method for obtaining Al vapor-deposited materials with excellent appearance, workability, and chemical conversion coatability.

[0002]

Prior art

The so-called vacuum vapor deposition method, in which a raw material is heated and vaporized in a vacuum or a dilute gas atmosphere and vapor-deposited onto a substrate, has the characteristics of greater degree of freedom in manufacturing method than that of the conventional electroplating and hot galvanizing method, and by heating and vaporizing a single raw material or simultaneous heating and vaporizing a mixture of raw materials, various alloy deposits, multilayer deposits, etc., can be relatively easily manufactured.

[0003]

Generally speaking, the heating-vaporization methods used in vacuum vapor deposition include resistance heating, high-frequency induction heating, electron-beam heating, ion beam heating, laser beam heating, arc discharge methods, etc., and they are properly used according to the type of raw materials, film-forming methods, etc. Among the heating methods, the vacuum vapor deposition method uses electron-beam heating and, because an electron beam has high energy and high energy density, the vaporization rate of the raw material can be made high, and it

is a heating method in which the surface of the raw material is directly irradiated (scanned) with electron beam; therefore, the heating efficiency (energy efficiency) is high and it is possible to easily vaporize various ceramic materials and metal which have high melting points and low vapor pressure. An electron beam can be easily deflected by magnetic field; therefore, it is possible to arbitrarily scan the surface of the raw material. Furthermore, for a number of raw materials it is possible to simultaneously heat and vaporize the respective raw material using an electron gun; therefore, we can easily manufacture various alloy deposits and multilayer deposits by vaporization of a number of raw materials. Thus electron-beam heating has various advantages and is one of the methods by which high productivity can be attained in continuous manufacturing of vapor-deposited materials.

[0004]

Incidentally, the corrosion resistance of Al and Al alloys is significantly than that of steel materials and, moreover, they are lightweight and have a clean appearance; therefore, they are widely used in construction materials, household electronic appliances and various kinds of containers. Al-plated steel sheets, which utilize such Al materials with excellent characteristics as plate layers, are also widely used in automobile exhaust systems, construction materials, various heat- and light-reflection materials and materials for constructing trash incinerators. Namely Al-deposited (or plated) steel sheets are surface-treated steel sheets obtained by depositing Al onto the surface of steel sheets.

[0005]

Hot dipping is commonly used as a method for industrial manufacture of Al-plated steel sheets. In hot dipping, steel sheets are dipped into a molten Al bath and passed through the Al bath; therefore, the temperature of the steel sheet after plating with Al is raised to approximately 700°C, so that we cannot avoid the formation of an Fe-Al intermetallic compound layer such as Fe_2Al_3 at the interface of the steel sheet and the Al plate layer. The intermetallic compound layer is fragile and therefore lacks processability when molten Al-plated steel sheets are subjected to high-degree molding. There are many cases in which the Al plates are detached from the steel sheets at their interface, thus there are problems in workability and corrosion resistance after processing.

[0006]

Therefore a small amount of Si was added to a molten Al bath to form an Al-Si plate containing approximately 10% Si, thereby the growth of the above-mentioned Fe-Al intermetallic compound layer was suppressed at the time of manufacture and, as a result, it has been adopted as

a means for improving the processability of molten Al-plated steel sheets. However, in this method with plated layers containing Si, it was impossible to improve the processability to completely eliminate the formation of the intermetallic compound layer. Furthermore, by the addition of Si to the Al plate, the corrosion resistance of the Al plate per se dropped, which is a new problem, thus it is very difficult to obtain a manufacturing method for Al-plated steel sheets with corrosion resistance after processing.

[0007]

On the other hand, for steel sheets Al-plated in an environment containing a large amount of halogen ions such as Cl^- ions, the passive films on the surface of the Al are easily destroyed and very often pitting corrosion occurs. White rust, with $\text{Al}(\text{OH})_3$, etc., as the main component of the corrosion products of Al, forms at the periphery of the pitting corrosion, and when the pitting corrosion progresses further towards the thickness of the steel sheet and reaches the steel sheet, red rust forms due to the corrosion of the steel sheet. The formation of such red rust and white rust remarkably damages the appearance of the Al-plated steel sheet and reduces the value of the product, thus it is undesirable.

[0008]

For the purpose of improvement of corrosion resistance of such molten Al-plated steel sheets, some molten Al alloy-plated steel sheets in which elements such as Zn were added to the Al plate have been also used. However, in the above-mentioned hot-dipping method, in the manufacturing method there is a large limitation in (a) the types of metal that are soluble in the Al baths, and (b) the amount of metals to be added to the Al baths; therefore, it is difficult to attain sufficient improvement in corrosion resistance.

[0009]

Accordingly, as aftertreatments of molten Al-plated steel sheets, improvement of corrosion resistance was also carried out by forming various chemical conversion films such as by chromating or thin-film organic resin-coating the surface of the plate. These aftertreatments have a large strong point in productivity from the viewpoint of being able to be carried out continuously in plating facilities for manufacturing molten Al-plated steel sheets. However, the films formed in the above-mentioned aftertreatments are very thin, so that they are easily damaged during handling or processing or by corrosion, thus defects and destruction of the films occur; therefore, reliable and effective improvement to corrosion resistance for molten Al-plated steel sheets is very scarce. Furthermore, forming organic resin coating adds the problems of the

working environment at the time of chromating, of Cr ion elution at the time of use, and of decreased weldability; therefore, there is a limitation to the uses, which is the present situation.

[0010]

On the other hand, because the above-mentioned problems can occur when Al-plated steel sheets are manufactured by hot-dipping method, the manufacture of Al-plated steel sheets by an electroplating method has been also studied and developed. Due to the problem of hydrogen overvoltage of Al per se, the electrodeposition of Al from aqueous solutions onto the surface of metal substrates is impossible. For the electrodeposition methods, electrodeposition from nonaqueous solutions prepared by dissolving various Al salts in nonaqueous organic solvents and electrodeposition from molten Al salt baths have been investigated. Compared with hot-dipping method, electroplating method has strong points which include (1) more types of metal can be added to the baths used, (2) a broader range for the amount of metal to be added to the baths used, and (3) not only pure Al electroplates but also various Al alloy plates can be electrodeposited onto the surface of metal substrates. And even when steel sheets are used as substrates, no fragile Fe-Al intermetallic compound can be formed at the interface of the steel substrate and the plate; therefore, Al-plated steel sheets with excellent processability can be obtained.

[0011]

However, generally speaking, the above-mentioned electroplating method is less efficient than the electrodeposition method from aqueous solutions, or the electrodeposition at high current density is impossible, which is a problem. Thus, in addition to the drawback of poor productivity, the plating baths are unstable electrically, thus there are many problems in putting the method to practical use at industrial scale.

[0012]

Contrary to the many problems with the hot-dipping method and nonaqueous electroplating method mentioned above, in vacuum vapor deposition, not only pure Al deposition but also deposition of various Al alloys can be carried out easily, and it has a strong point of being able to produce Al-plated steel sheets with good workability.

[0013]

Problems to be solved by the invention

As mentioned above, compared with the existing electroplating method and hot-dipping method, in the vacuum vapor deposition method many types of metal can be deposited and the

electron beam as a heating-vaporization source has a high energy density; therefore, when we think of continuous industrial production, it is advantageous in improvement of productivity.

[0014]

Incidentally, to carry out continuous industrial vacuum vapor deposition on a substrate, it is necessary to continuously introduce the substrate into a vapor deposition chamber while maintaining the vapor deposition chamber at specified vacuum, whereby the vapor of the raw material can be deposited onto the substrate surface. In industrial continuous production it is important to control the conditions for each manufacturing process; however, there are some cases in which there are products with one or at least two of the properties, including the adherence of the plate, processability, corrosion resistance after processing, chemical conversion, etc., are insufficient, which is a problem. In vapor deposition process there are various conditions and factors such as types of residual gas in the vacuum of the vapor deposition chamber and partial pressure of the gas, substrate temperature at the time of vapor deposition, pretreatment method and conditions of the vapor-deposited substrate, cooling method for the vapor-deposited substrate, etc. Therefore the technology for continuous and stable manufacture of products that satisfy the properties required for various Al vapor-deposited materials has not yet been established, thus further improvement of the quality of Al vapor-deposited products has been demanded.

[0015]

The object of the present invention is to solve the problems of the above-mentioned conventional methods by providing optimum manufacturing conditions for obtaining Al plated materials with stable quality in Al vacuum vapor deposition using electron-beam heating.

[0016]

Means to solve the problems

The method for manufacturing Al vapor-deposited materials of the present invention, which has attained the above-mentioned objective is that in the vacuum vapor deposition in which continuous Al vapor deposition is carried out on at least one side of a pretreated substrate, the essential points of the method simultaneously satisfy the following three conditions.

(1) the residual hydrogen gas content in the vapor deposition chamber is 90 vol% or greater, based on the total residual gas in the vapor deposition chamber,

(2) among the residual gas in the vapor deposition chamber, the sum of the partial pressure of moisture, oxygen, carbon monoxide, and carbon dioxide gas is 1×10^{-3} Pa or less, and

(3) the temperature T ($^{\circ}\text{C}$) of the substrate at the beginning of the vapor deposition satisfies the following condition

$$150^{\circ}\text{C} \leq T \leq 400^{\circ}\text{C}.$$

In addition, the present invention contains a method for pretreatment of the substrate. In the pretreatment method, the substrate is heated in a reducing gas atmosphere to carry out reduction and activation of the substrate surface, followed by cooling in a nonoxidizing atmosphere to the specified temperature; then the substrate is introduced into a vapor deposition chamber and Al vapor deposition of at least one side of the substrate is continuously carried out.

[0017]

There is no limitation to the vacuum vapor deposition method, as long as electron beam is used as the heating-vaporization source, and there is no limitation to the substrate to be deposited, thus the method is applicable to various metal substrates. In addition, there is no limitation to the shape of the substrates, thus laminar, rod-shaped, tubular substrates and materials machined to various other shapes can be used. In the following, explanation will be made using cold-rolled steel sheets as the substrates.

[0018]

Function

In the manufacture of Al vapor-deposited (or plated) steel sheets such as Al vapor-deposited steel sheets (in the following, "deposition" means "vapor deposition" unless otherwise specified), Al-Cr alloy-deposited steel sheets, Al-Ti alloy-deposited steel sheets, etc., the inventors of the present invention investigated the manufacturing conditions and the quality of the deposited sheets using the continuous vapor deposition apparatus shown in Figures 1 and 2.

[0019]

Figures 1 and 2 illustrate examples of continuous deposition apparatus. The cleaned steel belt substrate 1 is introduced into the vapor deposition chamber 6. The degree of vacuum in the vapor deposition chamber 6 is maintained at the desired vacuum by the combination of various vacuum pumps (not shown) through the evacuation pipe 22. In the vapor deposition chamber 6, raw materials 9 and 10 (at least one is Al raw material) are put in the vaporization tanks 11 and 12, the scanning irradiation of the surface of the raw materials 9 and 10 by the electron beam 8 generated from the electron gun 7 is carried out thereby the raw materials are heated and vaporized, thereby the desired Al vapor deposition is carried out on the bottom of the belt substrate 1. In case we want carry out vapor deposition of pure Al, we have to prepare only one Al raw material in the vapor deposition chamber. The degree of vacuum in the vapor deposition

chamber is monitored by the vacuum gauge 13, and the residual gas composition and their partial pressure are measured by the gas analyzer 14.

[0020]

It is known that, generally speaking, to obtain Al vapor-deposited steel sheets with good properties such as good adhesion, it is preferable to maintain as high degree of vacuum as possible inside the vapor deposition chamber. However, there are some cases in which controlling only the degree of vacuum cannot obtain good adhesion and deposition appearance, thus the inventors of the present invention investigated the effect of residual gas composition and gas ratio in the vapor deposition chamber on the manufacture of Al vapor-deposited sheets.

[0021]

As a result, it became clear that among the residual gas in the vapor deposition chamber, the necessary condition for obtaining stable Al vapor-deposited steel sheets with good properties requires that the sum of the partial pressure of moisture, oxygen, carbon monoxide, and carbon dioxide be 1×10^{-3} Pa or less at all times. Each of the four gas components, i.e., moisture, oxygen, carbon dioxide, and carbon monoxide (hereinafter these four gases are named generically "oxidizing gas"), contains at least one oxygen atom, and is therefore an oxidizing gas that brings about oxidation of the substrate surface prior to vapor deposition or oxidation of Al vapor deposit formed on the substrate surface. Accordingly, the sum of the partial pressure of moisture, oxygen, carbon monoxide, and carbon dioxide should be controlled to 1×10^{-3} Pa or less. If the oxidizing gases in the vapor deposition chamber are greater than 1×10^{-3} Pa, then reduction treatment of the substrate surface is carried out prior to Al vapor deposition, the oxidizing gases are adsorbed and reacted on the substrate surface, and thin reaction films, such as crystalline or amorphous oxide films or oxyhydrate films, are formed, which is undesirable. Especially in the case of carrying out vapor deposition on both sides of the substrate surface one after another using the vapor deposition apparatus illustrated in Figure 2, the residence time of the substrate surface to be deposited later in the vacuum is longer than that of the substrate surface on which deposition was carried out earlier; therefore, the above-mentioned oxide film is easier to grow, thus the adhesion and workability of the thus-obtained Al vapor-deposited steel sheet are not as good as those of the side that was deposited first.

[0022]

Furthermore, when such an oxidizing film is grown on the surface, if Al vapor deposition is carried out on such a surface, the adhesion of the deposit is reduced and, therefore, a portion of the deposit comes off from the interface of the substrate and the Al vapor deposit layer, which can

bring about the reduced processability of the products and, at the same time, a portion of the deposit layer can come off by processing, so the corrosion resistance at the area where the deposit layer came off is reduced, thus the desired corrosion resistance after processing cannot be obtained.

[0023]

Additionally, if a thin film, which is composed of an oxyhydrate film and an oxide film formed by adsorption/reaction of oxidizing gases, is not grown uniformly on the surface of the Al vapor deposit layer, irregular appearance results so that the value of the product drops remarkably. Moreover, if the surface or a portion of the surface of the Al vapor deposit layer is oxidized, crystalline or amorphous Al oxide(s) can form inside the deposit layer or on the surface of the deposit layer. Or, because the oxygen is solid-solubilized supersaturatedly in the deposit layer, strain can be generated in the crystal structure (crystal lattice) of the deposit layer, so that the hardness of the deposit layer itself can increase and, at the same time, the ductility becomes scarce so that if the Al vapor-deposited steel sheet is subjected to vigorous processing, the breakage, cracking, and flaking of the deposit layer can occur, thus the processability of the product and the corrosion resistance after processing are reduced.

[0024]

Therefore, in the present invention, we reduce the amount of oxidizing gas that remains in the vapor deposition chamber as much as possible. Namely, the control of the sum of the partial pressure of moisture, oxygen, carbon monoxide, and carbon dioxide among the residual gas in the vapor deposition chamber to 1×10^{-3} Pa or less is a necessary condition for reliable production of Al vapor-deposited steel sheets with good properties at all times.

[0025]

As for the residual gas components in the vapor deposition chamber, it is possible that there is a very small amount of oxidizing gas in addition to the above-mentioned four components. However, basically, unless we intentionally introduce a special oxidizing gas into the vacuum, the above-mentioned four gas components can be regarded as the oxidizing gas components in the vacuum; therefore it is sufficient to control the sum of the partial pressure of the four gases to 1×10^{-3} Pa or less.

[0026]

Next, in the present invention it is a necessary condition that the residual hydrogen gas content in the vapor deposition chamber be controlled to 90 vol% or greater based on the total

residual gas in the vapor deposition chamber. Hydrogen gas is a reducing gas therefore it does not exert such bad influence as that exerted upon by the aforementioned oxidizing gas but, on the contrary, by adsorption of the hydrogen on the substrate surface or deposit layer, it can suppress the adsorption/reaction of the oxidizing gas components. Namely, by the adsorption of hydrogen gas on the substrate prior to the vapor deposition, the substrate surface oxidation by the oxidizing gas can be prevented, which is useful for the maintenance of the substrate surface, which was cleaned and activated in the pretreatment process and, at the same time, by adsorption on the surface of Al vapor-deposited layer, the oxidation of the surface of the deposit layer by the oxidizing gas is prevented. As a result, attractive Al vapor-deposited products without irregular appearance can be obtained.

[0027]

In the present invention there is no limitation to the means for attaining the above-mentioned gas composition that remains in the vapor deposition chamber in the scope prescribed by the present invention. However, for example, the following method can be recommended.

[0028]

□ It is preferable to use a vacuum pump with a sufficiently large evacuation capacity that can maintain a high degree of vacuum in the vapor deposition chamber. This is because the higher the degree of vacuum in the vapor deposition chamber, naturally, the easier it is to reduce the sum of the partial pressure of the four kinds of oxidizing gases.

[0029]

□ It is preferable to reduce as much as possible (a) the vacuum leaks of the vapor deposition chamber or its accessory and piping and (b) the amount of leaking. This is a necessary condition for maintaining a high degree of vacuum and effectively prevents a leak-caused increase of the partial pressure of the oxidizing gas.

[0030]

□ It is preferable to sufficiently evacuate the gas from the vapor deposition chamber prior to conducting the vapor deposition. By lengthening the evacuation time, a high degree of vacuum can be obtained, and the amount of moisture discharged from the inner wall of the vapor deposition chamber can be reduced also at the time of the deposition.

[0031]

□ It is preferable to bake the inside of the vapor deposition chamber prior to carrying out vapor deposition. Prior to vapor deposition, we positively discharge the oxidizing gas, such as moisture, which was adsorbed by the inner wall of the vapor deposition chamber, into the vacuum by various heat treatments, thereby we can reduce the moisture content in the vacuum in advance.

[0032]

□ Panels and piping that were cooled by a cooling medium to very low temperature (-100°C or colder), the so-called cold trap, are introduced into an arbitrary place in the vapor deposition chamber or into the head part of the evacuation piping, which is an accessory to the vapor deposition chamber, and prior to vapor deposition or during the vapor deposition the residual oxidizing gas in the vacuum, such as moisture, is adsorbed, captured, and removed.

[0033]

□ Prior to the vapor deposition it is preferable to utilize the getter function of the Al vapor and Al-alloy vapor elements vaporized from the surface of the vaporization tank in order to capture the oxidizing gas remaining in the vacuum of the vapor deposition chamber by adsorption or reaction. Al is a metal that has a high affinity with oxygen and, therefore, by the getter function, the oxidizing gas can be captured effectively.

[0034]

□ The inside of the vapor deposition chamber is evacuated to a high degree of vacuum using the above-mentioned methods and, further, it is preferable to intentionally introduce hydrogen gas into the vacuum.

[0035]

Incidentally, the inventors of the present invention confirmed that, in addition to the condition of the above-mentioned residual gas components in the vacuum, the substrate temperature at the time of vapor deposition influences the quality of the obtained Al vapor-deposited steel sheets. Generally speaking, not limited to Al vapor deposition, but the temperature $T (^{\circ}\text{C})$ of the substrate at the time of various vapor depositions is adjusted to the specified range of temperature depending on various objectives, however, in the present invention from the viewpoints of adhesion of the deposit, guarantee of processability, good appearance of the deposit, color tone, prevention of the alloying of the deposit layer with the substrate, etc., it is a necessary condition that the temperature $T (^{\circ}\text{C})$ of the substrate at the time of vapor deposition be controlled to the condition $150^{\circ}\text{C} \leq T \leq 400^{\circ}\text{C}$.

[0036]

When the substrate temperature is lower than 150°C, the appearance of the deposit is dark gray and the glossiness and the brightness are reduced; also, even if the sum of the partial pressure of the oxidizing gas is less than 1×10^{-3} Pa, it is difficult to obtain an attractive appearance, which is undesirable. This is mainly caused by the influence of the substrate temperature on the size and orientation of the crystal grains deposited onto the surface of the Al vapor deposit layer formed on the substrate. When the substrate temperature is lower than 150°C, the crystal grains become fine and the unevenness of the deposit layer surface becomes significant, so that the light with wavelength in the visible region scatters on the surface of the deposit layer.

[0037]

When the substrate temperature is lower than 150°C, even if the partial pressure of gas in the vacuum of the vapor deposition chamber is within the above-mentioned prescribed range, sometimes there are cases in which the adhesion of the deposit layer and the processability may be reduced, depending on the amount of Al vapor deposited onto the steel sheet (especially Al alloy-deposited steel sheets), which is undesirable. The reason is presumed to be that the interfacial bonding force between the substrate and the Al deposit layer formed on the substrate surface is influenced by the substrate temperature, and if the temperature is lower than 150°C, the interfacial bonding force is insufficient.

[0038]

We can presume that another reason is that when the substrate temperature is low, strain is easily generated the crystal structure of the Al vapor deposit layer formed and, because the residual strain/stress becomes large, the ductility of the deposit layer drops. Thus, the Al vapor-deposited steel sheets obtained when the substrate temperature is lower than 150°C are subjected to strong molding, and breakage and cracking of the deposit layer can occur and, further, the deposited layer can fall off or peel off, which can lead to decreased processability and corrosion resistance after processing of the Al vapor-deposited steel sheets, thus it is necessary to control the substrate temperature to higher than 150°C.

[0039]

On the other hand, it is necessary to set the upper limit of the temperature T at 400°C. If Al vapor deposition is carried out at a temperature exceeding 400°C on a substrate, the substrate temperature after the vapor deposition exceeds 500-550°C and, especially in pure Al vapor-deposited steel sheets, there are cases in which an Fe-Al intermetallic compound layer is

formed at the interface of the pure Al deposit and the steel sheet, similar to that when hot dipping of steel sheet was carried out which is undesirable. When such an intermetallic compound is formed at the interface, and then an Al vapor-deposited steel sheet is strongly molded, due to weak interfacial bonding force between the deposit layer and the intermetallic compound layer, the deposit layer can be peeled, so the processability and corrosion resistance after processing are remarkably reduced.

[0040]

As described in detail in the above, in the method for manufacturing the Al vapor-deposited steel sheets of the present invention it is necessary that conditions simultaneously satisfy the following three conditions.

- (1) the residual hydrogen gas content in the vapor deposition chamber is 90 vol% or greater based on the total residual gas in the vapor deposition chamber,
- (2) among the residual gas in the vapor deposition chamber, the sum of the partial pressure of moisture, oxygen, carbon monoxide, and carbon dioxide gas is 1×10^{-3} Pa or less,
- (3) the temperature T ($^{\circ}\text{C}$) of the substrate at the beginning of the vapor deposition satisfies the following condition

$$150^{\circ}\text{C} \leq T \leq 400^{\circ}\text{C}.$$

If these three conditions are satisfied, it is possible to guarantee stably the adherence, processability, corrosion resistance after processing, and good appearance of Al vapor-deposited materials.

[0041]

In the method for manufacturing the Al vapor-deposited steel sheets of the present invention, it is preferable to carry out pretreatment of the substrate, i.e., clean and activate the substrate prior to vapor deposition. The pretreatment is necessary for securing good adhesion of the deposit layer of the Al vapor-deposited steel sheets. For the pretreatment, a suitable optimum treatment can be carried out depending on the materials of the substrates. For example, when the substrates are Al and Al alloys, alumite coating treatment can be carried out, and for other materials, degreasing and/or precoating after washing with acid, which is called very thin undercoating with good adhesion to the substrate, is carried out; therefore, it cannot be determined without consideration.

[0042]

As to the method for manufacturing the Al vapor deposited materials of the present invention, there is no limitation to the pretreatment method so that a suitable optimum

pretreatment method can be employed depending on the substrate materials. However, generally speaking, when the substrates are various steel sheets, we degrease the substrates, wash with acids, and then activate the substrate surfaces.

[0043]

One of the representative activation methods is ion bombardment using inactive ions such as Ar ions, nitrogen ions, etc., in vacuum. In this method, plasma of the above-mentioned gas is formed using various means, then the cationized gas in the plasma is collided at high speed with the substrate surface in order to bombard (sputter) the substrate surface, thereby removing the oxide films and the material adsorbed on the substrate surface. However, to obtain a sufficient activation effect by this method, a relatively long treatment time is needed, therefore in case we want to continuously manufacture vapor-deposited materials, the activation treatment becomes the rate-determining step and, as a result, the productivity of the Al vapor-deposited products drops remarkably, which is undesirable.

[0044]

In the present invention it is preferable to heat the substrate in a reducing gas atmosphere to carry out reduction and activation of the substrate surface. For the reducing gas, a mixture of nitrogen and hydrogen is preferably used. By heating the substrate to 600°C or higher in a reducing gas, the reduction and activation of the substrate surface can be carried out. After activation the substrate is cooled to the specified temperature in a nonoxidizing atmosphere and the substrate is then introduced into a vapor deposition chamber and vapor deposition is carried out, which is a preferable mode to carry into execution. By adopting the cleaning and activation pretreatment, the adherence between the Al vapor deposit layer and the substrate surface can be improved further and excellent processability and adherence of the deposit can be obtained.

[0045]

To introduce the substrate into the vapor deposition chamber while maintaining the surface condition of the substrate activated by cleaning pretreatment, it is necessary that the surface is not oxidized again. Accordingly, after reduction treatment is carried out, the substrate is cooled to the specified temperature in a nonoxidizing atmosphere and introduced into a vapor deposition chamber through a desired vacuum sealing apparatus where the nonoxidizing atmosphere was preserved.

[0046]

There is no limitation to the method for cooling the substrate after Al vapor deposition. However, by the radiant heat from the surface of the vaporization tank and latent heat and sensible heat from the vapor of metal raw material, the substrate temperature is raised considerably and, if at this state the substrate is transferred from the vacuum to the atmosphere through the specified vacuum sealing apparatus, there are some cases in which the desired properties cannot be obtained; therefore, it is preferable to go through a vacuum sealing apparatus under a dilute nonoxidizing atmosphere, and after it is sufficiently cooled in a nonoxidizing atmosphere it is then introduced into the air.

[0047]

If we introduce the Al vapor-deposited material at high temperature into the atmosphere, the surface Al of the deposit can react vigorously with the oxygen and the moisture in the air and form a very thin oxide film (passive film). If the substrate temperature is high, the growth of the oxide film can be accelerated. The oxide film that was grown to a thick film on the surface of the Al vapor-deposited substrate not only impairs the attractive appearance of the Al vapor deposit, but also causes a drop in the chemical conversion property, such as chromating treatment, thus it is undesirable.

[0048]

In the present invention, for example, if the substrate is a steel sheet and Al alloy deposition is carried out using a continuous vapor deposition apparatus illustrated in Figure 2, the processes can be carried out as follows: First of all, a steel sheet 1 is degreased by the degreasing apparatus 2 and is activated by the reducing gas furnace 3 containing an atmosphere of hydrogen-nitrogen mixed reducing gas. The activated steel sheet 1 is likewise cooled in the nonoxidizing cooling zone 4 of a reducing gas atmosphere and passes through the inlet-side vacuum sealing apparatus 5 of the dilute nitrogen gas atmosphere and is introduced into the first vapor deposition chamber 6. After one side (bottom side in the Figure) of the steel sheet 1 is deposited with Al vapor, it is introduced into the second vapor deposition chamber 17 through the intermediate chamber 15 and the opposite side of the steel sheet 1 is deposited with Al vapor. Then it passes through the exit-side vacuum sealing apparatus 18 containing a dilute nitrogen atmosphere and cooled sufficiently at the nonoxidizing cooling belt 19 within a nitrogen atmosphere, then it passes through the skin-pass roller 20 and is introduced into the aftertreatment apparatus 21. The first and the second vapor deposition chambers are adjusted to satisfy the prescribed conditions of the present invention. Other apparatus are not limited to those illustrated in Figure 2.

[0049]

By adopting the method for manufacturing Al vapor-deposited materials of the present invention it is possible to continuously produce products that satisfy various properties of Al vapor-deposited materials of the present invention. The present invention will be explained in further detail using the following application examples.

[0050]

Application examples

Application Example 1

The continuous vapor deposition apparatus shown in Figures 1 and 2 were used to manufacture pure Al vapor-deposited steel sheets by changing the vapor deposition conditions. The quality of the thus manufactured deposited materials was investigated. The main manufacturing conditions not shown in Table 1 are as follows:

[0051]

Main manufacturing conditions

Substrate: Ultra-low carbon Al-killed cold-rolled steel strip

Pretreatment of the substrate: Degreasing-washing with water-drying, then reduction/activation by heating the substrate in a hydrogen-nitrogen gas mixture atmosphere.

Hydrogen concentration: 5% (vol%)

Substrate temperature: 600°C or higher

Then the substrate was cooled to the specified temperature in H₂-N₂ gas mixture atmosphere

Content of vapor deposition: Pure Al vapor deposition

Degree of vacuum of the vapor deposition chamber: It was measured by a calibrated ionization vacuum gauge

Residual gas composition in the vapor deposition chamber: The ratio of the residual gas (composition) was measured by the following analytical apparatus.

Mass filter-type gas analyzer (MASSMATE-200 Model, ULVAC)

[0052]

Atmospheric conditions of inlet-side/outlet-side vacuum sealing apparatus: Ultra-low amount of oxygen and dilute nitrogen gas with ultra-low dew-point atmosphere

Oxygen content: 20 ppm or less

Dew point: -60°C

Heating source of raw material to be vaporized: Pias-type electron gun (maximum output power: 300 kW)

Vaporization tank: Electrically molten highly pure alumina vaporization tank (purity: 98% or greater)

(Only one was used) (equivalent to 11 in Figures 1 and 2)

Method for replenishing raw material to be vaporized: Pure Al wire (equivalent to A1050) is continuously fed to a molten Al bath by a wire feeder (purity: 99.7% or greater)

Method for cooling the substrate after vapor deposition: Cooled by ultra-low amount of oxygen and nitrogen gas with ultra-low dew point

Gas cooling: Circulating spraying mode

Oxygen content: 20 ppm or less

Dew point: -60°C

[0053]

The following properties of the pure Al vapor-deposited steel sheets obtained under the above-mentioned manufacturing conditions were evaluated.

1. Tests for the adherence and processability of the deposit

□ Cellophane tape was stuck on the ball-impacted part of a test piece, then the amount of the deposit on the peeled tape was visually estimated.

□ A test piece was bent 180° , then cellophane tape was stuck to the bent part, then the amount of the deposit on the peeled tape was visually estimated. The above-mentioned two tests were carried out and then evaluated as follows:

O: The deposit has excellent adherence. In the two tests, the deposit flaking or peeling is not observed.

Δ: The adherence of the deposit is slightly poor. At least in one of the tests a slight deposit flaking or peeling was observed.

X: The adherence of the deposit is poor. In at least one of the two tests, significant deposit flaking or peeling is observed.

[0054]

2. Investigation of surface appearance

Non-uniform color and its extent of the oxide film on the deposit surface were visually evaluated in the length and width directions of the deposit and then the following judgment was made.

O: There is no non-uniform color, it is glossy and it is excellent in appearance.

Δ: The non-uniform color is almost not significant but the gloss of the non-uniform color region is slightly low and the appearance is slightly poor.

X: The non-uniform color is significant, the gloss of the non-uniform color region is considerably low and the appearance is poor.

The results thus obtained and the results of the comparative materials are shown together in Table 1.

[0055]

Table 1

No.		① 純Alめ 付着量 (g/m ²)	② 蒸着 室 真空 度 ($\times 10^{-2}$ Pa)	③ 蒸着室内残留ガス成分 H ₂ H ₂ O+O ₂ +CO ₂ +CO (%) (%) $\times 10^{-4}$ Pa			④ めっき 時の被 めっき 基温度 (°C)	⑤ 性能評価 めっき 密着性 めっき 外観		⑧ 特記事項
⑨ 実 例	1	20	1.5	94.8	3.7	5.6	160	○	○	
	2	"	1.5	94.8	3.7	5.6	200	○	○	
	3	"	1.6	94.4	4.0	6.4	250	○	○	
	4	"	1.6	94.4	4.0	6.4	300	○	○	
	5	"	2.0	95.2	3.5	7.0	350	○	○	
	6	"	2.0	95.2	3.5	7.0	380	○	○	
	7	30	0.9	97.8	1.1	1.0	150	○	○	
	8	"	1.2	97.5	1.5	1.8	200	○	○	
	9	"	1.7	93.8	4.6	7.8	250	○	○	
	10	40	1.0	97.6	1.3	1.3	150	○	○	
	11	"	1.4	96.0	2.8	3.9	200	○	○	
⑩ 比 較 例	12	20	1.7	92.1	6.1	10.4	300	○	△	
	13	30	2.0	91.6	6.8	13.6	200	△	△	
	14	"	2.5	84.4	13.4	33.5	250	△	△	
	15	"	4.0	37.3	13.4	33.6	200	△	×	
	16	"	8.0	20.5	17.5	140.0	200	×	×	
	17	20	10.0	15.5	18.4	184.0	200	×	×	
	18	"	1.3	95.3	2.8	3.6	100	△	△	
	19	"	2.0	92.0	6.0	12.0	100	△	△	
	20	30	7.0	23.4	16.3	107.1	100	×	×	
	21	40	1.0	97.0	1.8	1.8	100	△	×	
	22	30	0.9	97.7	1.1	1.0	450	×	×	
例	23	40	1.3	96.4	2.5	3.3	450	×	×	⑪ めっき界面に Fe-Al金属間 化合物層生成 し加工性低下
	24	30	1.9	92.5	5.4	10.3	450	×	×	
	25	"	6.0	25.0	13.4	80.4	450	×	×	

⑫ ⑫ H₂ガス (%) は、全真空度に対する vol体積%を意味する。
 (H₂O+O₂+CO₂+CO)ガス成分の合計値(Pa)は、全真空度×(各ガス成分のモル合計%)で算出。

- Key:
- 1 Amount of pure Al deposited
 - 2 Degree of vacuum in vapor deposition chamber
 - 3 Residual gas components in vapor deposition chamber
 - 4 Substrate temperature at the time of deposition
 - 5 Evaluation of properties
 - 6 Adherence of the deposit
 - 7 Appearance of the deposit
 - 8 Especially noteworthy
 - 9 Application Example
 - 10 Comparative Example

- 11 Fe-Al intermetallic compound was formed at the interface of the deposit and the processability was reduced
- 12 Note: H₂ gas (%) is vol% based on the total degree of vacuum.
The sum of the partial pressure of (H₂O + O₂ + CO₂ + CO) (Pa) was calculated by the total degree of vacuum x (sum of mol% of all gas components).

[0056]

From Table 1 it is clear that when the ratio of the residual gas components in the vapor deposition chamber and the substrate temperature at the time of vapor deposition prescribed in the present invention are simultaneously satisfied (Nos. 1-11), excellent adherence and appearance of the deposits can be obtained. On the other hand, even if only one of the above-mentioned three conditions is outside the prescribed scope (Nos. 12-25) the adherence of the deposits and the appearance of the deposits are poor. Especially when the degree of vacuum in the vapor deposition chamber is low (the residual gas pressure is high) and the proportion of hydrogen gas in the residual gas is very small (Nos. 15-17, 20, and 25) both the adherence of the deposits and the processability are inferior and, among them, when the substrate temperature at the time of vapor deposition is low and outside the prescribed scope of the present invention (No. 20), or in the case wherein the substrate temperature is high (No. 25), the two properties are very inferior.

[0057]

Application Example 2

Al alloy vapor-deposited steel sheets were manufactured using the continuous vapor deposition apparatus shown in Figure 2 and by changing the vapor deposition conditions shown in Table 2. The quality of the thus manufactured Al alloy vapor-deposited steel sheets was investigated. The main manufacturing conditions excluding those shown in Table 2 are as follows: The degree of vacuum of the vapor deposition chamber and the residual gas composition were measured as in Application Example 1.

[0058]

Main manufacturing conditions

Substrate: Ultra-low carbon Ti-killed cold-rolled steel sheet

Pretreatment of the substrate: Same as Application Example 1

Content of vapor deposition: Al alloy vapor deposition (types and amount deposited are shown in Table 2).

Atmospheric conditions for inlet-side/outlet-side vacuum sealing apparatus: Same as Application Example 1

Heating source for vaporization of raw material: Same as Application Example 1.

[0059]

Vaporization tank: Vaporization tank for Al bath (equivalent to 11 in Figures 1 and 2)

Vaporization tank made of molten alumina with high purity (purity: 98% or greater)

Vaporization tank for Cr (this is used at the time of deposition of Al-Cr alloy deposits and is equivalent to 12 in Figures 1 and 2).

Vaporization tank made of graphite (sealing material)

And a mode was adopted in which a Zr-Cr alloy bath was formed in the vaporization tank and from the alloy bath only Cr was selectively vaporized.

Vaporization tank for Ti (this is used at the time of deposition Al-Ti alloy deposits and is equivalent to 12 in Figures 1 and 2).

Vaporization tank made of graphite (sealing material)

Method for replenishing the raw material for vaporization: Al raw material

Pure Al wires (equivalent to A1050) were continuously fed to a molten Al bath by a wire feeder (purity: 99.7% or greater)

Cr raw material

Cr briquette was continuously fed to the above-mentioned Zr-Cr alloy bath by a briquette feeder (purity: 99.7% or greater)

Ti raw material

Pure Ti wires were continuously fed by a wire feeder (purity: 99.7% or greater)

Method for cooling the substrate after vapor deposition: Same as that of Application

Example 1.

[0060]

The evaluation of the following properties was carried out for the various Al vapor-deposited steel sheets obtained under the above-mentioned manufacturing conditions.

1. Tests for adherence of the deposits and processability

The contents of the tests and the standards for judgment are the same as those of Application Example 1.

2. Chemical conversion

Al alloy vapor-deposited steel sheets were skin-pass rolled, followed by coating-type chromating treatment, then the appearance of the surface was visually evaluated.

O: Excellent in chemical conversion

There was no non-uniformity in chromating and uniform chromate films were obtained.

Δ: Slightly poor in chemical conversion

Non-uniform chromating caused by non-uniform deposited surface was slightly generated.

X: Inferior in chemical conversion

Non-uniform chromating caused by non-uniform deposited surface was considerably generated.

[0061]

3. Corrosion resistance after processing

The test piece was subjected to (a) drawing by an Erichsen tester and (b) cross cut from the surface of the deposit by a cutter knife, then the test piece was subjected to aqueous salt solution spray test. The time it took to generate 1% red rust on the deposited steel sheets was evaluated.

O: Excellent in corrosion resistance after processing

Slightly poorer when compared with the time taken to generate 1% red rust on an unprocessed test piece.

Δ: Slightly poor in corrosion resistance after processing

Red rust was formed in less than half the time it took to form 1% red rust on an unprocessed test piece.

X: Considerably poor in corrosion resistance after processing

Red rust was formed on the processed region in early stage.

The results obtained and the results of comparative materials are shown together in Table 2.

[0062]

Table 2

No.		① めっき内容		④ 蒸着室真空度 ($\times 10^{-2}$ Pa)	⑤ 蒸着室内残留ガス成分			⑥ めっき時のめっき温度 ($^{\circ}$ C)	⑦ 性能評価			⑩			
		② 種類および組成	③ 付着量 (g/m ²)		H ₂ (%)	H ₂ O+O ₂ +CO ₂ +CO (%)	$\times 10^{-4}$ Pa		⑧ 密着性	⑨ めっき外観	加工後耐食性				
⑪	実施例	1 Al-10%Cr	20	1.4	95.2	3.4	4.8	200	○	○	○				
		2 "	"	1.6	94.5	3.7	5.9	300	○	○	○				
		3 "	"	1.8	96.0	2.9	5.2	400	○	○	○				
		4 Al-15%Cr	30	1.5	95.5	3.0	4.5	300	○	○	○				
		5 Al-20%Cr	40	2.0	95.2	3.5	7.0	150	○	○	○				
		6 Al-20%Cr	"	0.8	97.9	1.0	0.8	250	○	○	○				
⑫	比較例	7 Al-20%Cr	20	2.0	90.5	7.7	15.4	300	○	△	△				
		8 "	30	3.0	70.0	19.7	59.1	200	△	△	△				
		9 "	"	9.0	19.4	21.4	182.6	250	×	×	×				
		10 Al-15%Cr	20	1.3	95.7	2.8	3.6	100	△	△	△				
		11 Al-5%Cr	30	1.0	97.5	1.8	1.8	450	△	△	△				
		12 Al-10%Cr	20	1.9	90.5	7.4	14.1	100	△	△	△				
		13 Al-10%Cr	"	6.0	24.5	22.8	182.4	100	△	×	△				
		14 Al-5%Cr	40	1.3	9.2	21.6	28.1	450	×	×	×				
⑪	実施例	15 Al-5%Ti	20	0.9	97.9	1.1	1.0	200	○	○	○				
		16 Al-10%Ti	30	0.8	97.0	1.8	1.4	300	○	○	○				
		17 Al-5%Ti	40	0.9	97.7	1.1	1.0	400	○	○	○				
⑫	比較例	18 Al-5%Ti	30	1.3	95.4	2.5	3.3	100	△	△	△				
		19 Al-3%Ti	40	1.0	95.2	3.4	3.4	450	△	×	△				
		20 Al-15%Ti	20	2.0	91.0	6.4	12.8	250	○	△	○				
		21 "	"	1.9	90.9	6.1	11.6	100	△	△	△				
		22 "	"	1.9	90.9	6.1	11.6	450	△	×	△				
		23 "	30	4.0	35.7	13.1	52.4	300	×	×	×				
		24 Al-10%Ti	20	10.0	14.6	18.9	189.0	300	×	×	×				
		25 Al-10%Ti	"	7.0	19.4	18.3	128.1	100	×	×	×				
		26 Al-5%Ti	40	8.0	18.4	28.3	228.4	450	×	×	×				

- Key:
- 1 Content of deposition
 - 2 Type and composition
 - 3 Amount deposited
 - 4 Degree of vacuum of vapor deposition chamber
 - 5 Residual gas composition in the vapor deposition chamber
 - 6 Substrate temperature at the time of deposition
 - 7 Evaluation of properties
 - 8 Adherence
 - 9 Appearance of deposits
 - 10 Corrosion resistance after processing
 - 11 Application Example
 - 12 Comparative Example

[0063]

From Table 2 it is clear that when Al-Cr alloy vapor-deposited steel sheets and Al-Ti alloy vapor-deposited steel sheets were manufactured under the manufacturing conditions prescribed in the present invention (Nos. 1-6 and Nos. 15-17), the adherence of the deposits, chemical conversion, and the corrosion resistance after processing are all excellent. On the other hand, the Al-Cr alloy vapor-deposited steel sheets (Nos. 7-14) and the Al-Ti alloy vapor-deposited steel

sheets (Nos. 18-26), which were manufactured under the conditions that at least one of (a) the ratio of the residual gas and (b) the substrate temperature was outside the prescribed scope of the present invention, at least one of the above-mentioned properties is inferior.

[0064]

Effect of the invention

The present invention is constituted as described above and in continuous manufacture of Al vapor-deposited steel sheets, by controlling the residual gas composition and the substrate temperatures at the time of deposition, products with excellent adherence of the deposits, appearance, and chemical conversion can be obtained reliably.

Brief description of the figures

Figure 1 shows equipment for continuous vapor deposition

Figure 2 shows equipment for continuous vapor deposition

Explanation of symbols

- 1: Substrate
- 2: Degreasing apparatus
- 3: Gas reducing furnace
- 4: Nonoxidizing cooling zone
- 5: Inlet-side vacuum sealing apparatus
- 6: (First) vapor deposition chamber
- 7: Electron gun
- 8: Electron gun
- 9: Vaporization raw material A
- 10: Vaporization raw material B
- 11: Vaporization tank A
- 12: Vaporization tank B
- 13: Vacuum gage
- 14: Gas analyzer
- 15: Intermediate chamber
- 16: Deflector roll
- 17: Second vapor deposition chamber
- 18: Outlet-side vacuum sealing apparatus
- 19: Nonoxidizing cooling zone
- 20: Skin pass roll

- 21: Aftertreatment apparatus
- 22: Evacuation pipe
- 23: Table roll
- 24: Intermediate chamber.

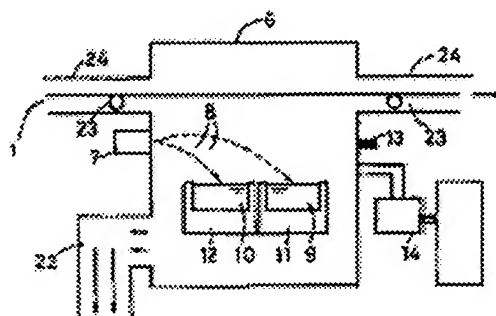


Figure 1

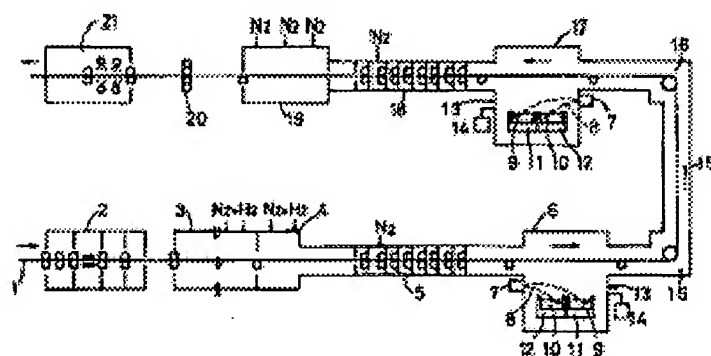


Figure 2